mmole) of acid IIa in 7 ml of acetic anhydride was heated for 10 min at 120°C, 0.55 ml (5 mmole) of 58% perchloric acid, and the mixture was then heated for another 40 min. It was then cooled, and the dye was removed by filtration and crystallized. The yield was 1.9 g.

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THIAZOLO(OXAZOLO)THIENO[b]PYRIMIDINES.

PREPARATION FROM 2-ALLYLTHIO(OXY)THIENO[2,3-d]PYRIMIDINES AND HYDROLYSIS

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Heterocyclization of 5,6-disubstituted 2-allylthio(oxy)-4-oxothieno[2,3-d]-pyrimidines by treatment with halogens affords thieno[3,2-e]thiazolo[3,2-*a*]-pyrimidine iminium salts. Treatment of these salts with aqueous sodium acetate results in cleavage of the thiazoline ring.

Pyrimidines condensed with the thiophene or thiazole nucleus are important members of the numerous heteroatomic bicyclic systems. The best known are the thienopyrimidines [1], which include many compounds showing a wide spectrum of biological activity [2]. Representatives of another type of binuclear heterocycles with two nitrogen atoms and one sulfur atom, the thiazolo[2,3-b]pyrimidines, also display various types of biological activity [3], and have therefore attracted the attention of many workers [4, 5].

Tricyclic systems in which the pyrimidine ring is condensed simultaneously with thiophene and thiazole nuclei are virtually unknown as a result of the lack of convenient methods for the preparation of thiazolothieno[b]pyrimidines. Retrosynthetic analysis, examination of the various routes to thiazoles and thiophenes, and assessment of the availability of the required starting materials suggested that the most logical route to these tricyclic systems should include annelation of the pyrimidine and thiazole rings. In such a case, convenient precursors would be 2-thio-4-oxothieno[2,3-d]pyrimidines, which have become

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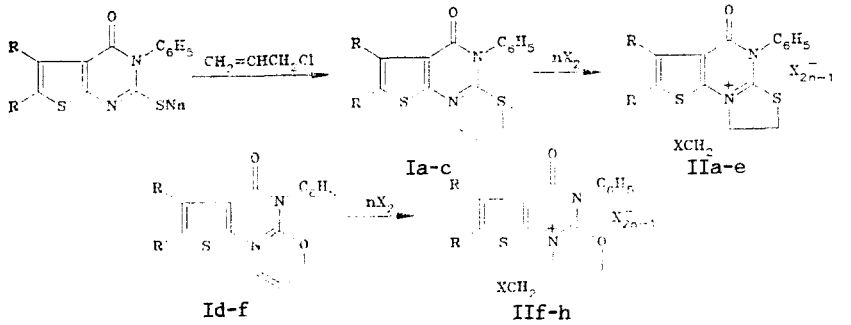
available by methods which we have developed [6, 7]. Condensation of these compounds with α-haloketones or dibromoethane gives a mixture of isomers differing in the position of ring coupling [8]. A similar outcome was seen on treating 2-allylthiothieno[2,3-d]pyrimidines with bromine or iodine [9]. It is also noteworthy that the absence of regiodirectivity is also seen in analogous systems containing an oxazole rather than a thiazole ring.

The object of the present investigation was to examine the electrophilic cyclization of 2-allylthio(oxy)thieno[2,3-d]pyrimidines with halogens to give polyheterocycles with the thiazolo(oxazolo)thieno[b]pyrimidine structure, and to study some of their properties.

The starting materials for these studies were the 2-allylthio(oxy)thieno[2,3-d]pyrimidines (Ia-f), obtained from the sodium salts of the appropriate 2-thio(oxo) derivatives and allyl chloride, as in [6, 7]. Their homogeneity was checked to chromatography, and their composition and structure by elemental analysis and the PMR and IR spectra (Table 1). The UV spectra of the S- and O-allyl compounds were in accordance with the spectra of the corresponding thieno[2,3-d]pyrimidine sodium salts, which have the thiol and enol structures with a negative charge on the sulfur or oxygen atom in the 2 position [6, 7]. It may therefore be concluded that alkylation of the sodium salts with allyl chloride takes place at the sulfur or oxygen atom, to give (Ia-f).

In order to close the thiazole ring, we decided to employ electrophilic cyclization, which is used extensively, for example, in the preparation of thiazolo[2,3]pyrimidines [4, 10]. The electrophilic reagents used were bromine or iodine. Treatment of (Ia-f) with these in nonpolar solvents, for example, chloroform or carbon tetrachloride, resulted in resinification of the reaction mixture. However, the reaction occurred smoothly in oxygen-containing solvents such as ethanol, acetic acid, or dioxane, at 20-25°C, resulting in all cases in the formation of a single product. The yields of the products (and the conversion of the starting materials) were strongly dependent on the amount of halogen added. When the molar ratio of halogen to allyl compound was 1:1, the product yields were 30-50%, while increasing this ratio to 2:1 (or 3:1 in the case of iodine) gave near-quantitative yields.

All the reaction products were isolated as crystalline solids, which were sparingly soluble in nonpolar organic solvents and were brightly colored, the color depending on the halogen used (the bromo-compounds were bright yellow, and the iodo-compounds dark red). The products were salts, since the halogen incorporated in the anion was quantitatively determined by titration with sodium thiosulfate. The titration data showed an unusual feature, bromination giving salts with a tribromide anion, and iodination the triiodides or in some instances the pentaiodides. It is noteworthy that the heterocyclization of S-allyl derivatives of pyrimidines has hitherto been carried out using equimolar amounts of halogen, and irrespective of the complexity of the heterocyclic systems, the formation of the monobromides and monoiodides only has been reported [4, 9, 10]. On the basis of the elemental analyses, PMR and IR spectra (Table 2), the cationoid moiety is assigned the structure 6,7-disubstituted 1,2-dihydro-1-halomethyl-4-phenyl-5-oxothieno[3,2-e]thiazolo-[3,2-a]pyrimidinium, which forms the basis of the iminium salts (IIa-h).



I a, d, II a, b, f, g R+R=$(CH_2)_4$; I b, e, II c, h R+R=$(CH_2)_3$; I c, f, II d, e R=R=CH_3; II a, d, h X=I, n=2, b, e, g X=Br, n=2, c, f, X=I, n=3

The IR spectra of (IIa-h) show absorption for the carbonyl group at 1700-1710, the iminium group at 1330-1340, and for CH_2X at 580 and 710 cm^{-1}. The PMR spectra of (IIa-i) contain no signals for olefinic protons, but show a multiplet for the methine proton at

TABLE 1. Properties of 2-Allylthio(oxy)-3-phenyl-4-oxo-5R,6R-thieno[2,3-d]pyrimidines (Ia-f)

Compund	Empirical formula	mp, °C*	R_f**	IR spectrum, cm^{-1}			PMR spectrum, ppm					Yield, %
				C=O	C=N	C—Z—C***	R+R	CH_2S; CH_2O, d	$=CH_2$, t	=CH, m	C_6H_5, m	
Ia	$C_{19}H_{18}N_2OS_2$	185...186	0,8	1680	1520	720	1,84 m, 2,76 m, 2,94 m	3,76	5,12	5,86	7,45	85
Ib	$C_{18}H_{16}N_2OS_2$	212...213	0,9	1670	1530	720	2,20...3,30 m	4,02	5,12...6,15		7,98	67
Ic	$C_{17}H_{16}N_2OS_2$	179...180	0,85	1690	1530	720	2,38 s, 2,41 s	3,76	5,12	5,86	7,50	73
Id	$C_{19}H_{18}N_2O_2S$	140...141	0,72	1690	1530	1233	1,84 m, 2,76 m, 2,94 m	4,15	5,26	5,86	7,45	80
Ie	$C_{18}H_{16}N_2O_2S$	125...127	0,65	1695	1530	1233						90
If	$C_{17}H_{16}N_2O_2S$	116...117	0,85	1690	1530	1233	2,33 s, 2,41 s	4,15	5,26	5,85	7,50	73

*Compounds (Ia, d-f) were recrystallized from ethanol, and (Ib, c) from dioxane.
**Eluent, dioxane–ethanol, 1:1.
***(Ia-c), Z = S, (Id-f), Z = O.

TABLE 2. Properties of 1-Halomethyl-4-phenyl-5-oxo-1,2-dihydrothieno[3,2-e]thiazolo[3,2-*a*]pyrimidinium Salts (IIa-i)

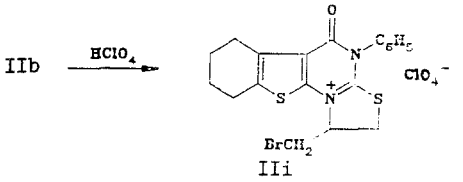
Compound	Empirical formula	mp, °C (decomp.)	IR spectrum, cm^{-1}		PMR spectrum, ppm					Yield, %
			C=O	C=N	R+R* (2 m)	CH_2X, d	CH_2Si; CH_2O, d	CH, m	C_6H_5, m	
IIa	$C_{19}H_{18}I_4N_2OS_2$	209...210	1710	1633	1,78; 2,82	3,72	4,09	5,74	7,54	85
IIb	$C_{19}H_{18}Br_4N_2OS_2$	193...194	1710	1630	1,78; 2,83	3,90	4,12	5,70	7,50	100
IIc	$C_{18}H_{16}I_6N_2OS_2$	101...103	1710	1630						75
IId	$C_{17}H_{16}I_4N_2OS_2$	142...143	1710	1630						90
IIe	$C_{17}H_{16}Br_4N_2OS_2$	158...159	1710	1625						90
IIf	$C_{19}H_{18}I_6N_2O_2S$	96...98	1710	1630						55
IIg	$C_{19}H_{18}Br_4N_2O_2S$	124...125	1710	1625	1,70; 2,80	3,91	4,01	5,30	7,50	77
IIh	$C_{18}H_{16}I_4N_2O_2S$	91...93	1710	1630						81
IIi	$C_{19}H_{18}BrClN_2O_5S_2$	227...228	1730	1630	1,86; 2,92	4,18 (4H)		5,90	7,85	

*The PMR spectra of (IIc-f, h) could not be obtained as a result of their low solubility.

5.3-5.9 ppm and a doublet for the CH_2X proton at 4.0-4.2 ppm. Signals for the CH_2S (or CH_2O) groups are seen at 3.8-4.2 ppm, i.e., virtually the same as in the starting materials (Ia-f). Two maxima are seen in the UV spectra of (IIa-j), at 230-245 nm (log ε 3.8-4.6) and 280-320 nm (log ε 2.8-3.4).

These findings confirm the structures of (IIa-h) as systems containing angularly condensed rings, and exclude the alternatives, such as linearly condensed isomers, the formation of which has been reported previously [8, 9]. The cyclization of (Ia-f) to (IIa-h) only is due to the fact that in the concluding step of electrophilic addition of halogen at the double bond of the allyl residue, only one of the nitrogen atoms of the pyrimidine ring can function as a nucleophile, namely that remote from the carbonyl group. The nucleophilicity of the heteroatom adjacent to the carbonyl group is evidently considerably reduced by the presence of the phenyl substituent, which enhances the delocalization of the lone pair of the nitrogen atom. These factors are responsible for the regioselective heterocyclization of the allyl compounds (Ia-f) to the thiazolothieno[b]pyrimidinium salts [IIa-h].

The properties of the iminium salts obtained were examined. Compounds (IIa-h) were stable to strong protonic acids. On prolonged heating of salt (IIb) with an excess of perchloric acid in DMSO, the cationoid heterocyclic residue remained unchanged, and 95% of a colorless crystalline compound was isolated, which from its spectral properties and elemental analysis was the perchlorate (IIi). Specifically, the IR spectrum of this salt showed strong absorption at 1100 cm^{-1} which is characteristic of ionic perchlorates.

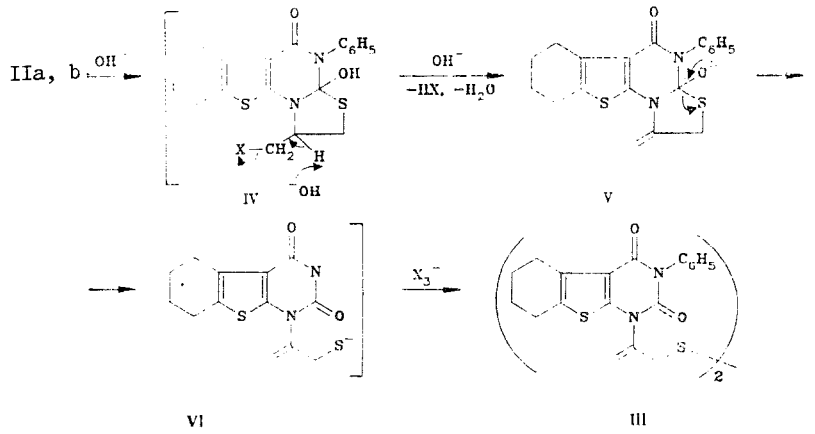


IIi

The presence of an iminium fragment in (IIa-h) gives reason to expect that these compounds will be highly reactive towards nucleophilic reagents and bases. Only a few examples of the reactions of tricyclic condensed thiazolium salts with nucleophiles have been reported [11-14]. In some instances, nonselective ring cleavage occurs [11, 13], while in others stable pseudobases are formed [13, 14]. It was this difference which, among others, led us to examine the reactivity of the salts obtained here. Another reason was the presence in the compounds (II) of other groups reactive towards acids and bases, in addition to the inimium group. For these reasons, a study of the side reactions of the salts (II) was of considerable interest.

The studies showed that the iminium salts (IIa-h) are extremely sensitive to bases. For instance, treatment of these compounds even with weak (10-20%) aqueous solutions of alkali resulted in considerable resinification, no identifiable reaction products being obtained. However, treatment of (IIa, b) with 20% aqueous sodium acetate in DMSO at 25°C gave near-quantitative yields of the same compound, pure by TLC, and giving colorless monocrystals on crystallization from dioxane. The use of spectral methods alone did not enable its structure to be determined reliably, and therefore it was subjected to x-ray structural examination,* which showed conclusively that the compound obtained was the disulfide (III). The formation of (III) may be represented by a sequence of reactions. Initially, nucleophilic attack of the hydroxide ion on the carbon of the iminium group in (IIa, b) gives the pseudobase (IV), an important distinguishing feature of which is the presence of four heteroatomic substituents at carbon. In the presence of excess base, hydrogen halide is eliminated and the hydroxy group deprotonated, resulting in the appearance of a double bond and the O-anion (V). Stabilization of the latter is effected by the formation of a carbonyl group and cleavage of the C–S bond, generating the thiolate anion (VI). In the final stage, this anion is oxidized by the trihalide anion to give the disulfide (III).

*The molecular and crystal structure were determined by Yu. T. Struchkov (Institute of Heteroorganic Compounds, Academy of Sciences of the USSR) with K. A. Potekhin and A. V. Maleev (Vladimir Pedagogical Institute). Complete results will be published separately.



The high preparative yields of (III), and the absence of other reaction products, indicates the exclusive selectivity of this multistage reaction, distinguishing compounds of this type (II) from other trinuclear thiazolium salts [11-13].

The reaction of 2-allylthio(oxo)-4-ketothieno[2,3-d]pyrimidine with halogens thus provides a general method for the preparation of thieno[3,2-b]thiazolo(oxazolo)[3,2-*a*]pyrimidines in high yields using a simple procedure.

EXPERIMENTAL

IR spectra were obtained on an IKS-29 spectrometer in KBr disks, and PMR spectra on a Tesla 60 MHz spectrometer in $CDCl_3$ (Ia-g) and DMSO-D_6, internal standard TMS. UV spectra were recorded on an SF-26 instrument in alcohol, concentration 10^{-4} M. The elemental analyses for Hal, N, and S were in agreement with the calculated values.

The characteristics of compounds (Ia-f) and (IIa-i) are given in Tables 1 and 2.

2-Allylmercapto-3-phenyl-4-oxo-3,4,5,6,7,8-hexahydrobenzo[b]thieno[2,3-d]pyrimidine (Ia). A mixture of 3.4 g (10 mmole) of the sodium salt of 3-phenyl-4-oxo-3,4,5,6,7,8-hexahydrobenzo[b]thieno[2,3-d]pyrimidine [7], 11.6 g (15 mmole) of allyl chloride, and 50 ml of ethanol was boiled for 1 h. The solid which separated on cooling was filtered off, washed a few times with water, and recrystallized from alcohol to give 3 g of (Ia).

Compounds (Ib-f) were obtained similarly.

1-Iodomethyl-4-phenyl-5-oxo-1,2,6,7,8,9-hexahydrobenzo[b]thieno[3,2-e]thiazolo[3,2-*a*]-pyrimidinium Triiodide (IIa). To 0.35 g (1 mmole) of (Ia), dissolved with heating in 20 ml of glacial acetic acid, was added a solution of 0.8 g (3 mmole) of iodine in 30 ml of acetic acid. After 5 min, a solid began to separate. The mixture was kept for 3 h at 25°C, then heated to the boil, and filtered hot. The solid was washed several times on the filter with glacial acetic acid and ether to give 0.72 g (86%) of (IIa) mp 209-210°C (decomp.).

When the reaction was carried out in ethanol for 24 h, the yield of (IIa) was 70%, and in dioxane, 80%.

Compounds (IIc, d, f, h) were obtained similarly.

1-Bromomethyl-4-phenyl-5-oxo-1,2,6,7,8,9-hexahydrobenzo[b]thieno[3,2-e]thiazolo[3,2-*a*]-pyridinium Tribromide (IIb). Compound (Ia) (0.35 g, 1 mmole) was dissolved with heating to 70°C in 20 ml of glacial acetic acid. The mixture was then cooled to 25°C, 0.32 g (2 mmole) of bromine in 5 ml of glacial acetic acid added, and the mixture kept for a day. The solid was filtered off, and washed on the filter several times with acetic acid, followed by ether to give 0.57 g (10%) of (IIb), mp 193-194°C (decomp.).

Compounds (IIe, g) were obtained similarly.

1-Bromomethyl-4-phenyl-5-oxo-1,2,6,7,8,9-hexahydrobenzo[b]thieno[3,2-e]thiazolo[3,2-*a*]-pyrimidinium Perchlorate (IIi). To a solution of 1 g (1.5 mmole) of (IIb) in DMSO was added dropwise 15 ml of perchloric acid. The mixture was heated for 2.5 h, and the solid which separated was filtered off and washed on the filter with alcohol and ether to give 0.57 g (95%) of (IIi), mp 227-229°C (decomp.).

Solvate of [2-(3-Phenyl-2,4-dioxo-5,6,7,8-tetrahydrobenzo[b]thieno[2,3-d]pyrimid-1-yl)-propen-3-yl] Disulfide (III) with Dioxane. To a solution of 1.5 g (1.7 mmole) of the salt

(IIa) in 50 ml of DMSO was added dropwise with ice-cooling 20 ml of 20% aqueous sodium acetate, followed by 50 ml of water. The solid which separated was filtered off, and washed with water and methanol. Recrystallization from dioxane gave 0.6 g of the solvate of (III) with dioxane, mp 227°C.

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SYNTHESIS OF TETRAORGANO-SUBSTITUTED SILANES WITH THE BENZO[b]THIOPHENE MOIETY

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Catalytic dehydrocyclization of dimethyl(o-tolyl)- and dimethyl-4-(m-xylyl)-(benzo[b]thien-2-yl)silanes has given 11,11-dimethyl and 8,11,11-trimethyl-6,11-dihydro-11-silabenzo[b]naphtho[2,3-d]thiophenes, which were oxidized to the ketones. Previously unknown diorganobis(benzo[b]thien-2-yl)silanes have been obtained.

Organosilylated benzo[b]thiophenes have received little attention [1-4]. The availability of the starting benzo[b]thiophene, obtained in high yield from ethylbenzene and hydrogen sulfide over a chromium catalyst [5], has permitted silicon-containing compounds of this type, which are novel with respect to the nature of the substitution at the silicon atom, to be examined.

It has previously been shown possible [6] to carry out the catalyzed dehydrocyclization of organo-substituted silanes over chromic oxide catalysts. We here report the catalytic synthesis of some representatives of this new class of heterocyclic compounds containing the benzo[b]thiophene fragment (I) and a silicon atom in the ring. X-ray crystal

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